The Refractivity of CO_2 Under Simulated Martian Conditions

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The refractivity of carbon dioxide has been measured at 2.26 gHz under simulated Martian conditions, and at standard temperature and pressure. In the temperature range of 150 to 190°K, at pressures from 2 to 25 millibars, the refractivity per molecule per cm^3 is 1.78×10^{-17} ± 0.06 when scaled by the ideal gas law. The measurements include pressures and temperatures which are within 3°C of the sublimation curve. This result is slightly lower than the best measurements previously obtained near standard temperature and pressure at other frequencies (1.8345×10^{-17} ± 0.0003) and at 2.26 gHz under standard conditions by the authors (1.8413×10^{-17} ± 0.005). It is concluded that the scaled refractivity of CO_2 in the range of temperatures and pressures stated above may be a few percent lower than under standard conditions. These results do not significantly alter the conclusions regarding the atmosphere of Mars as measured by the radio occultation method.

1. Introduction

The evolution of planetary space probes has resulted in the emergence of radio occultation experiments as the principal tool for the remote sensing of planetary atmospheric structures. As the space probe moves behind a planet, the propagation path connecting it with the earth passes through successively lower portions of the planetary atmosphere. The resulting atmospherically induced phase and amplitude perturbations are recorded for later study. Under certain conditions,

these data may be used to deduce an atmospheric refractivity profile.

Hypothesized model atmospheres may then be tested by direct comparison

of their computed refractive properties (Kliore et al, 1965) or, assuming

the constituents are known, by integral equation techniques (Fjeldbo

and Eshleman, 1968).

In the case of the Mariner IV experiments performed at Mars, the

models inferred for the lower atmosphere range from 100% CO_2 at a few

millibars pressure to 80% CO_2, 20% N_2 at slightly lower pressures.

Martian surface temperatures apparently range from about $150^{\circ}K$ at the

winter pole where the atmosphere is in equilibrium with the solid CO_2

phase, to perhaps $270^{\circ}K$ for the summer day. Specifically, Mariner IV

gave the results of $160^{\circ}K$ at 4.5 mb for Electris on a late winter day

and about $230^{\circ}K$ at 8 mb pressure for Mare Acidalium in late summer at

night. Over Electris, the atmosphere is very nearly isothermal, while

over Mare Acidalium, the temperature decreases steadily with increasing

altitude. Surface topography, specifically the altitude of the occulting

feature, may account for the differences in surface pressure (Fjeldbo

and Eshleman, 1968). These results correspond to atmospheres which are

considerably thinner and colder than those deduced by other methods

(de Vaucouleurs, 1954; Kaplan et al, 1964).

While many factors enter into the interpretation of the occultation

data, a physical constant which directly affects these particular results

is the refractivity of CO_2. The occultation experiments at Mars performed

so far, and those presently planned for the future, have been conducted

on frequencies very close to 2300 MHz. As the dielectric properties

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of CO_2 apparently had not been measured at this frequency and under conditions remotely similar to those which exist on Mars, an experimental determination of these properties was undertaken.

It is concluded that the refractivity of CO_2 is 1.78 ± 0.06 x 10^{-17} molecules/cm^3 in the temperature range of 150 to $190^{o}K$, and for pressures ranging from about 2 to 25 mb. This value is slightly lower than that previously reported at standard temperature and pressure by other authors (Newell and Baird, 1965; Essen and Froome, 1951). However, the difference is at the limit of resolution of the present experiment so that the statistical significance of this result is difficult to determine.

The authors also determined the refractivity near 2300 MHz under ambient laboratory conditions with results which are in agreement with the previous determinations.

The remainder of this paper discusses the experimental techniques and data reduction procedures employed to determine the value given above.

2. Theory of Measurement

The refractive index of a gas is the ratio of the velocity of light in a vacuum to its velocity with the gas present. At microwave frequencies the most convenient method for determining refractive index is to measure the change in resonant frequency of a cavity as the gas is introduced (Newell and Baird, 1965). Then

$$n = \frac{c}{v} = \frac{f_v}{f_g}$$

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where f_v = frequency in vacuum

f_g = frequency with gas present

Refractivity, N, is a derived value equal to $(n - 1) \times 10^6$, or

$$N \times 10^{-6} = (n - 1) = \frac{f_v - f_g}{f_g}$$

The refractivity may be attributed to the gas parcel in the cavity, and described as a function of temperature and pressure, or, alternatively the refractive effects may be divided among all the molecules present. In the latter case the effects are expressed as refractivity per molecule per unit volume. Since the number density of an ideal gas is given by

$$\rho = \frac{1}{k} \frac{p}{T},$$

where p is pressure, T is absolute temperature and k is Boltzmann's constant, normalized refractivity is $N \cdot kT/p$.

In the past refractivity has been measured under ambient laboratory conditions and the results corrected to standard temperature and pressure. These results are then further scaled to Martian conditions by occultation workers. Our purpose was to determine the validity of this procedure. In keeping with this motivation we sought to achieve sufficient accuracy to eliminate imperfections in our knowledge of the properties of CO_2 as the possible source of the discrepancies between the results of the occultation experiments and those employing other techniques. This implied a minimum measurement accuracy of about ± 0.2 N-units under Martian conditions. This in turn required a measurement of the change in cavity resonant frequency when the gas was introduced

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consisting of about ± 1 part in 10^7. Since it is difficult to construct a cavity in which the half power width of the resonance wave is less than about 1 part in 10^5 of the resonance frequency, measurements to 0.01 this width were required.

The measurement problem was aggravated by the temperature range required for the experiment. For a cavity constructed of homogeneous materials, the rate of change of frequency with temperature is very close to the thermal coefficient of expansion of the metal used. Even for a cavity constructed of invar (coefficient of expansion $= 0.8 \times 10^{-6}/^{o}C$), a 1.0 degree Celius temperature change would mask the expected effects of CO_2. The drifting temperature techniques described later were adopted since the effects of temperature over the range of interest could be minimized only with great difficulty.

3. Equipment Description

The dimensions of the cavity were selected to provide a variety of transverse electric field modes in the vicinity of 2300 MHz. Physically, the cavity was machined from a 0.5" wall brass pipe, 10" in diameter and 10" long. The end plates were also brass, of 0.75" thickness, secured with screws every 15°. Both the cylinder and the end plates were silver plated to increase surface conductivity. Intimate thermal contact between the end plates and the cylinder was assured by the use of fine gage indium wire in the joint. Cooling was accomplished by circulating liquid nitrogen through a twenty-turn copper coil soldered to the outer cavity wall. Loop coupling was used to minimize excitation of degenerate TM modes. The experimental

setup showing the cavity is shown in Fig. 1.

The cavity was surrounded by a thermal blanket consisting of fifty layers of aluminized mylar and mounted in a steel vacuum chamber. Two dual-stage vacuum pumps were used, one for evacuating the chamber and the other to continuously pump an oil manometer used for pressure measurements in the 2 to 25 mb range. A conventional thermocouple gage was employed in the 1 to 100 micron pressure range. Carbon dioxide gas was admitted either directly to the vacuum chamber through a valve manifold or via a sample bulb whose volume was approximately 1/400th of the system volume. The gas entered the cavity through two 60° sectors, 0.1" deep, cut in the top of the brass cylinder which served the dual function of suppressing degenerate transverse magnetic modes.

Two thermocouples, one in each end plate, were used for both absolute temperature measurement and to indicate the temperature differential across the cavity. It was assumed that gas inside the cavity was at the cavity temperature.

The electronic system was driven by a quartz oscillator having a daily stability better than 5 parts in 10^{10}. Two coherent frequency synthesizers were used to phase lock a klystron signal generator which then drove a 1-watt TWT amplifier. This relatively high power permitted the external loading on the cavity to be minimized. Coupling, both in and out, was effected through loops inserted in waveguide-beyond-cutoff holes in the top plate. Very loose coupling together with silver plating of the cavity produced an operating Q of 113,000 in the TE_{013} mode at 2258 MHz.

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The cavity was used as a transmission type bandpass filter. Its resonance curve was displayed on an oscilloscope and compared with an identical curve drawn on the face of the display tube. Once the curves were matched by changing synthesizer frequency, the sweep could be stopped precisely at the resonance peak. The center frequency was then read directly from a counter whose time base was derived from the master quartz oscillator. Using this curve matching technique, it was possible to repeat measurements of cavity center frequency to ± 200 Hz.

The gas used in the experiment was Liquid Carbonic, L-119, medical grade CO_2. This gas was subject to a quality control procedure which involved continuous monitoring of impurities during manufacture, and spot checks of the gas after it was placed in the bottle. The estimated error due to the maximum impurities, principally air and water vapor, was less than 0.1%

4. Measurement Procedure

The thermal time constant of the cavity-vacuum chamber system is about 9 hours. Over a period of time which is short compared with this time constant, the rate of cavity expansion is very nearly linear.

The experimental technique adopted was to establish the frequency drift of the cavity, insert a fixed quantity of gas and then determine the resulting shift in frequency drift characteristics. The offsets between two successive pairs of frequency drift curves was due to the increase in dielectric material in the cavity.

The procedures employed were as follows: first, the cavity was flushed with CO_2, cooled below the lowest temperature of interest,

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and evacuated to at least 25 microns Hg. No measurements were taken until the temperature gradient across the cavity stabilized. A sequence of temperature, pressure and frequency measurements was used to establish the rate of change of the various quantities. A bulb of gas would then be admitted and the next sequence of measurements started immediately, with a constant 15 seconds delay between the last reading in one sequence and the first in the next. The gas charge was inserted immediately (within 1 or 2 seconds) after the last reading in each sequence.

Figures 2, 3 and 4 illustrate the resulting frequency changes. The format for all three is the same, but each covers a different range of temperature. Line segments have been matched to the associated data points by the least squares error method. The conditions under which these measurements were made, and their relationships to the Martian atmosphere, are given in the pressure/temperature diagram of Fig. 5. Here, the lettered pressure changes correspond to the frequency changes in Figs. 2, 3 and 4. The range of possible Martian atmospheres is indicated by the dotted area. Mariner IV provides a good measure of the pressure. Ten millibars is taken as an approximate upper bound, and provides some margin for variations in pressure with elevation of features on Mars. The temperature is bounded on the left by the sublimation curve for CO_2 (Hilsenrath et al, 1960) and loosely on the right by the Mariner occultation emersion results.

The pronounced change in slope between the first and second segments of each plot is due to a change in system thermal time constant with the first admission of CO_2. After that the slope remains relatively

constant since the thermal conductivity of a gas is independent of
pressure once sufficient molecules are present to exceed the molecular
flow regime. The slight decrease in the slope steepness between the
initial segments with gas present and the last segment of a sequence
reflects an exponential approach of the cavity temperature to equilibri-
um. There is also a tendency for the slope of the second segment to be
intermediate to the slope in vacuum and that of the segments immediately
following. This effect is due to the gas having an intermediate value
of thermal conductivity before the pressure independent regime is reached.

Except for the first charge of gas in each run, the precise time
for evaluating the differences was not critical since the lines between
any two sequences were very nearly parallel. However, for the first
charge of gas, the results were very sensitive to the time of evaluation
because of the marked change in slopes. Furthermore, the first point
in the second sequence of each run consistently lay below the line which
best fits the remainder of the points in the sequence. It is impossible
to determine whether this discrepancy was due to gross error, a change
in the properties of CO_2, or some unknown instrumental effect associated
with the apparatus. This was the only place where a detectable systema-
tic departure from the best fitting line occurred. In reducing the data,
all the differences were evaluated at the first point in each sequence,
i.e., 15 seconds after the gas was admitted. In most cases the time of
evaluation could be moved several minutes in either direction without
significantly altering the results.

5. Results

The results of these measurements are presented in Table 1. As before, the lettered conditions and values correspond to pressure and temperature changes depicted in Figs. 2 through 5. No values are given for points M and N because the charging bulb was improperly flushed, leading to the possibility of CO_2 being diluted with air for these two points. However, there is no reason for rejecting the two remaining points after the frequency drift pattern had been reestablished.

The approximate errors for each measurement are indicated. These are based upon the estimated standard deviation of the differences between the straight line segments computed in the usual way, using the deviations of each set of data points from the associated line to obtain the statistics of that segment. There was considerable variation in how well each line segment fit the associated data points, and this was reflected in the variations of estimated errors among the results.

A typical calculated error in the measurement of cavity resonant frequency was $\pm$ 250 Hz (or $\pm 5\%$), a value which agrees well with the accuracy to which various operators could reset the controlling synthesizer under static conditions. A constant error of $\pm 4\%$ was added to account for the uncertainties in reading the oil manometer. Since the temperature was determined to a small fraction of one percent, it was not considered in the error calculations. The weighted averages given at the bottom of the table were obtained by summing all of the data, and using the estimated statistical signal-to-noise ratio as the coefficient for each term. The average, excluding A and B, was obtained following the same procedure but leaving out the first two

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points. The authors have considered various sources of systematic error but believe that because the results are based entirely upon measurements of differences that such errors are probably quite small. It was therefore concluded from this experiment that a refractivity per molecule per cm^3 of 1.78 x 10^{-17} ± 0.06 is most probable. On the basis of Gaussian statistics the error implies an approximately 80% chance that the true value is less than that reported under standard conditions at other frequencies.

Consequently, two measurements were made under ambient conditions at 1.84 and 2.26 gHz to allow us to distinguish between the effects of frequency and those of rarification at low temperature. Such measurements also provided a check for possible experimental bias. Values of 1.8379 and 1.8413 ± 0.005 were obtained at these two frequencies. The principal error source is the determination of barometric pressure.

Table 2 provides a comparison of the CO_2 refractivity measurements which have been made thus far. With the exception of the 48 gHz experiment (Newell and Baird, 1965), the tabulated values are taken from Essen and Froome (1951). Values for dielectric constant have been converted to refractivity by

$$n = \varepsilon^{1/2},$$

neglecting magnetic permeability. The quantities given in the table are obtained by dividing the refractivity under standard conditions by the molecular density of 2.68612 x 10^{19} molecules/cm^3, corresponding to those conditions. At or near standard conditions there is no significant change in the refractive power of CO_2 over a very wide range of

frequencies. The value obtained under simulated Martian conditions represents the only appreciable deviation, and the significance of this deviation is itself subject to speculation.

6. Conclusions

At standard temperature and pressure the close agreement between the refractivity of CO_2 at all frequencies strongly suggests that there are no large systematic errors in the experiment. Under Martian conditions there is the possibility that the refractivity per molecule is slightly reduced relative to laboratory conditions, when scaled by the ideal gas law. Unfortunately, the deviations of CO_2 from the ideal gas law apparently have not been measured in the range of pressure and temperature of interest here, so it was not possible to base the computations on experimentally verified number densities.

If one takes a three standard deviation bound as an absolute limit on the error, then the per-molecule refractivity under Martian conditions is almost certainly (0.997 probability) within about $\pm 10\%$ of the standard temperature and pressure value. From a geophysical point of view this variation is unimportant to the understanding of the Martian atmosphere.

7. Acknowledgment

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Table 1

Refractivity of CO_2 at 2.26 gHz

Pressure Change	(N-units/molecule/cm^3x10^{17})	Temperature $\emptyset^\circ K$	Pressure mb
A	$1.98 \pm 14\%$	146.8	2.4
B	1.89 ± 15	149.8	5.0
C	1.80 ± 13	152.4	7.6
D	1.75 ± 11	155.2	10.1
E	1.70 ± 11	157.9	14.4
F	1.71 ± 16	163.2	2.9
G	1.79 ± 16	165.2	5.6
H	1.79 ± 9	167.5	8.1
I	1.71 ± 15	169.5	10.6
J	1.78 ± 13	171.8	13.1
K	1.78 ± 8	173.9	17.8
L	1.84 ± 16	183.5	4.9
M	–		
N	–		
O	1.92 ± 7	187.5	20.2
P	1.70 ± 8	189.7	25.2

Weighted average 1.78 ± 0.06 if all points taken

$1.77 \pm \underbrace{0.06}_{formal}$ if A and B neglected

Table 2

Carbon Dioxide

Frequency		Conditions	(N-units/molecule/ cm^3) x 10^{17}	Author	Date
0.5	MHz	Ambient	$1.8416 \pm ?$	Watson	1934
1.0	MHz	Ambient	1.8383 ± 0.004	Hector and Woernley	1946
1844	MHz	Ambient	1.8379 ± 0.005	Tyler and Howard	1969
2258	MHz	Ambient	1.8413 ± 0.005	Tyler and Howard	1969
2263	MHz	Simulated Martian	1.78 ± 0.06	Tyler and Howard	1969
9000	MHz	Ambient	1.8391 ± 0.004	Lyons, Birnbaum and Kryder	1948
9000	MHz	Ambient	1.8346 ± 0.006	Birnbaum, Kryder and Lyons	1951
24000	MHz	Ambient	1.8391 ± 0.004	Essen and Froome	1951
48000	MHz	Ambient	1.8435 ± 0.0003	Newell and Baird	1964

8. References

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Figure Captions

1. Diagram of Experimental Apparatus

2. Frequency Drift Curves, Run 1

3. Frequency Drift Cruves, Run 2

4. Frequency Drift Curves, Run 3
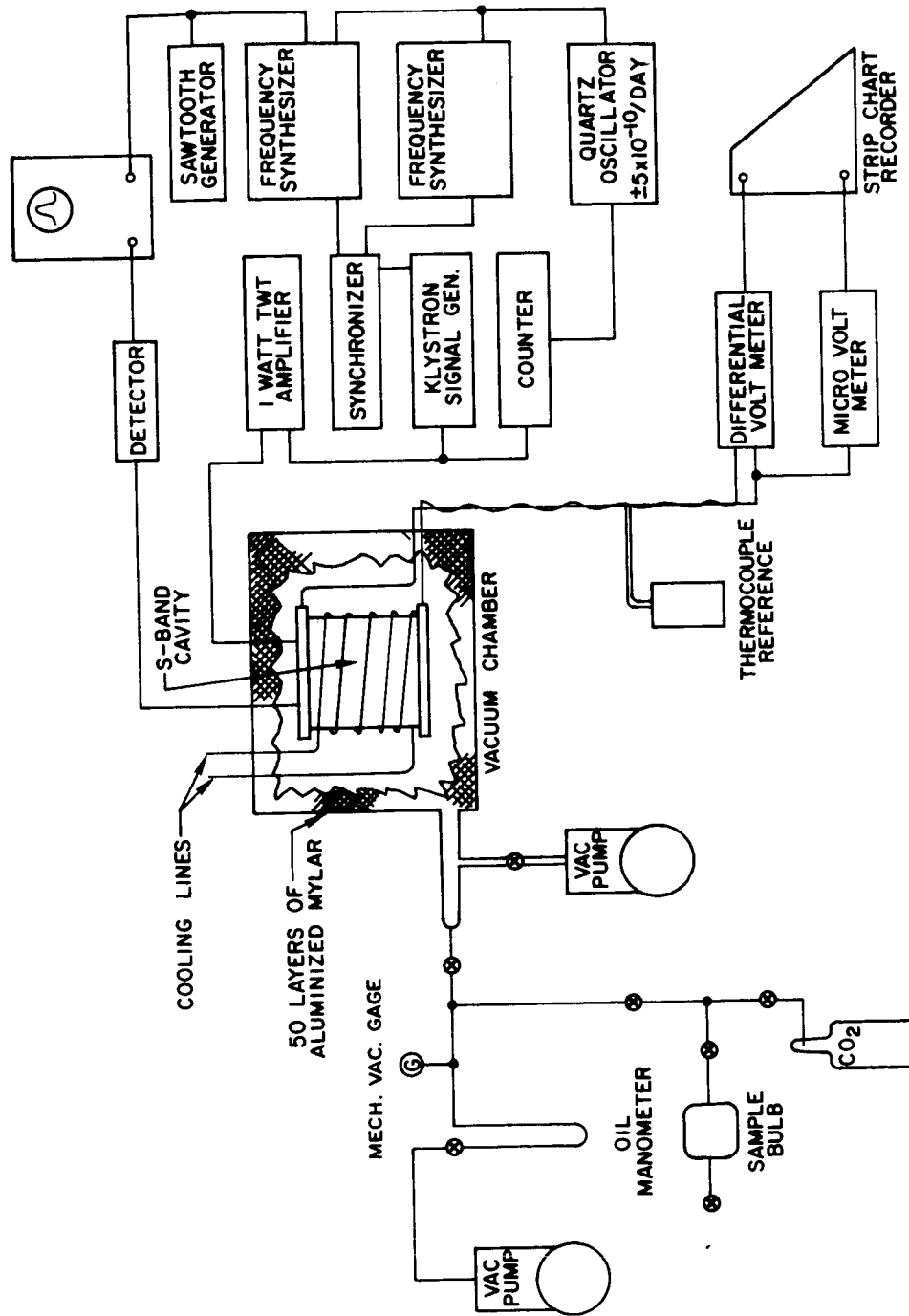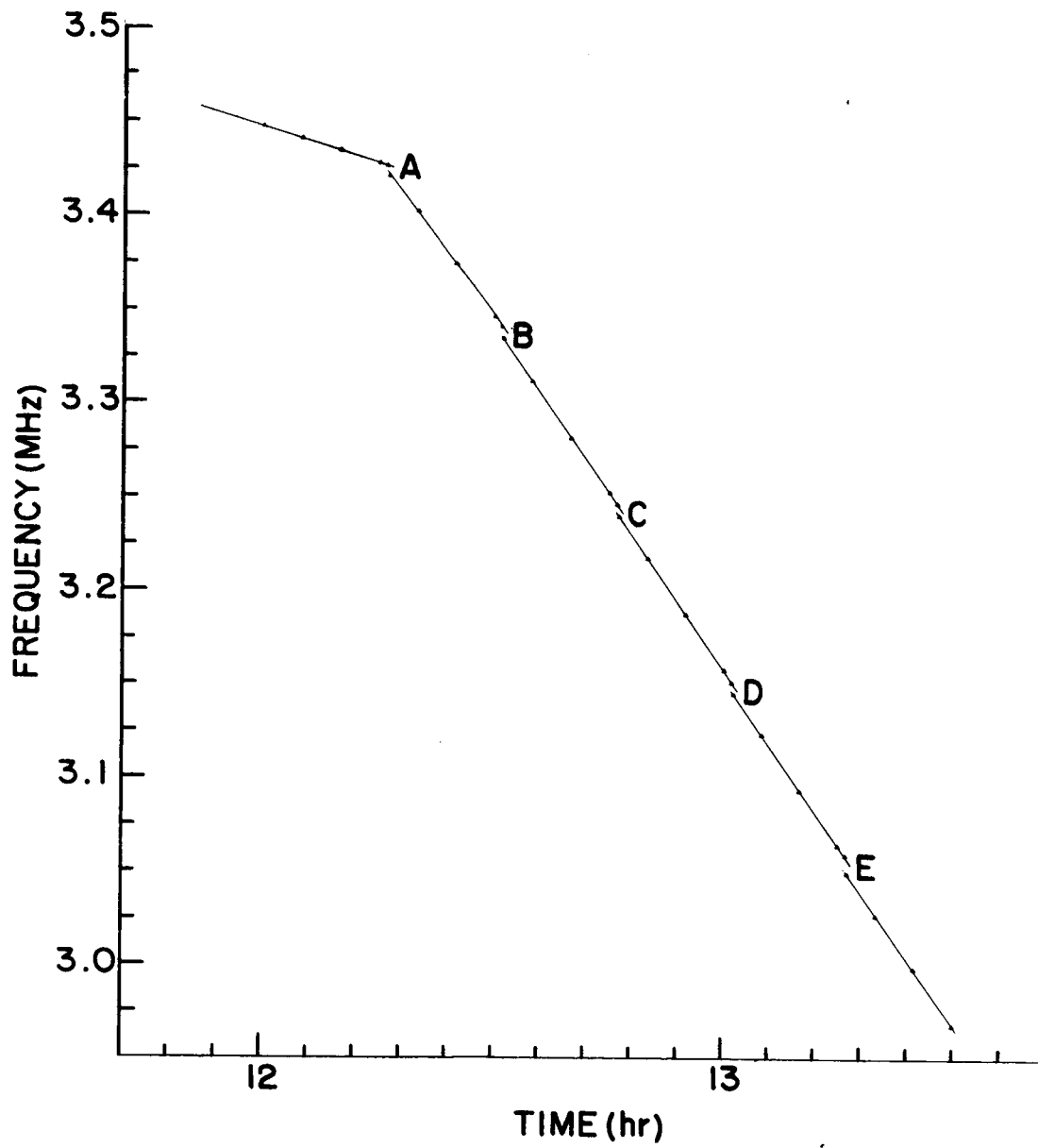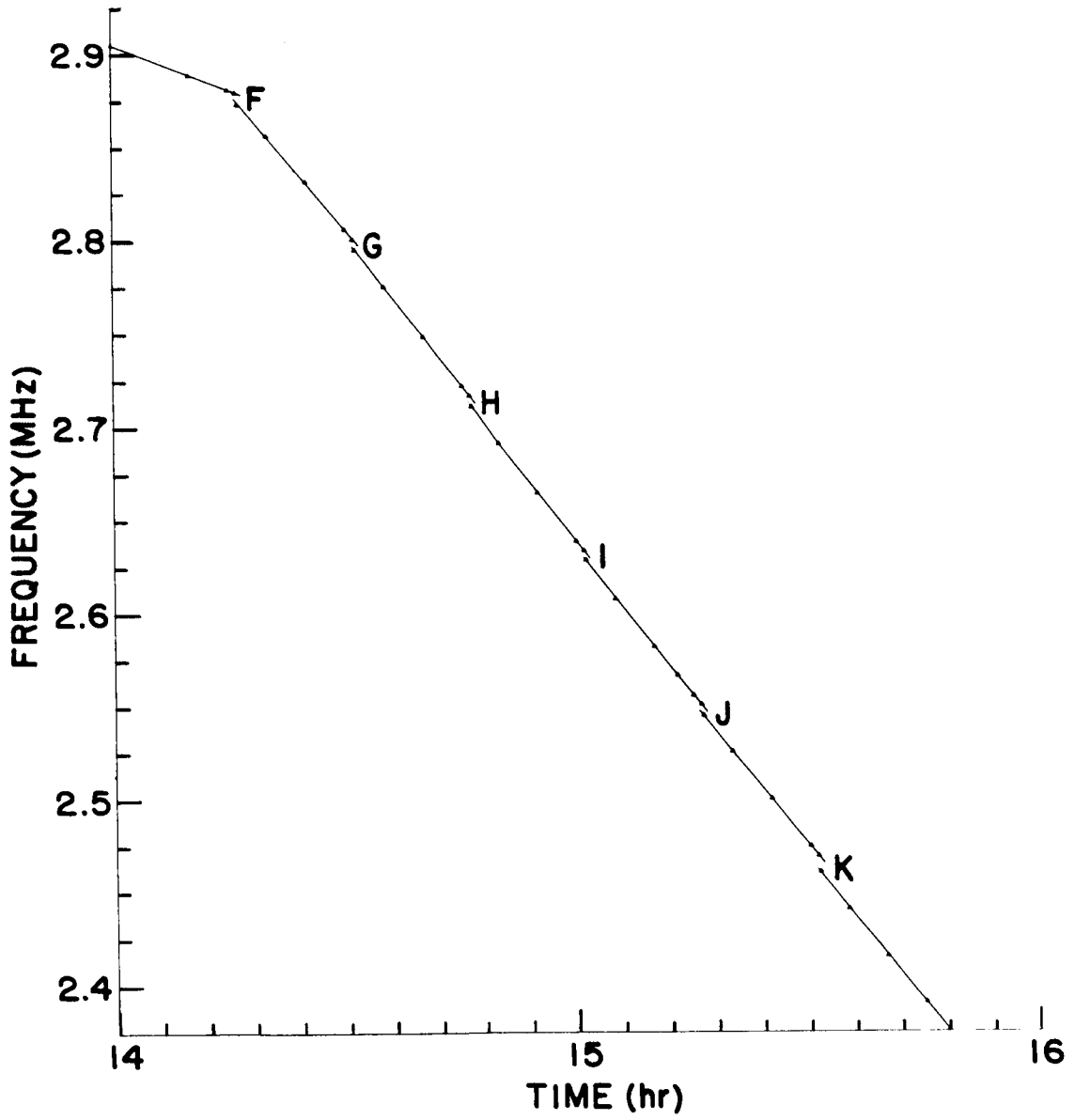
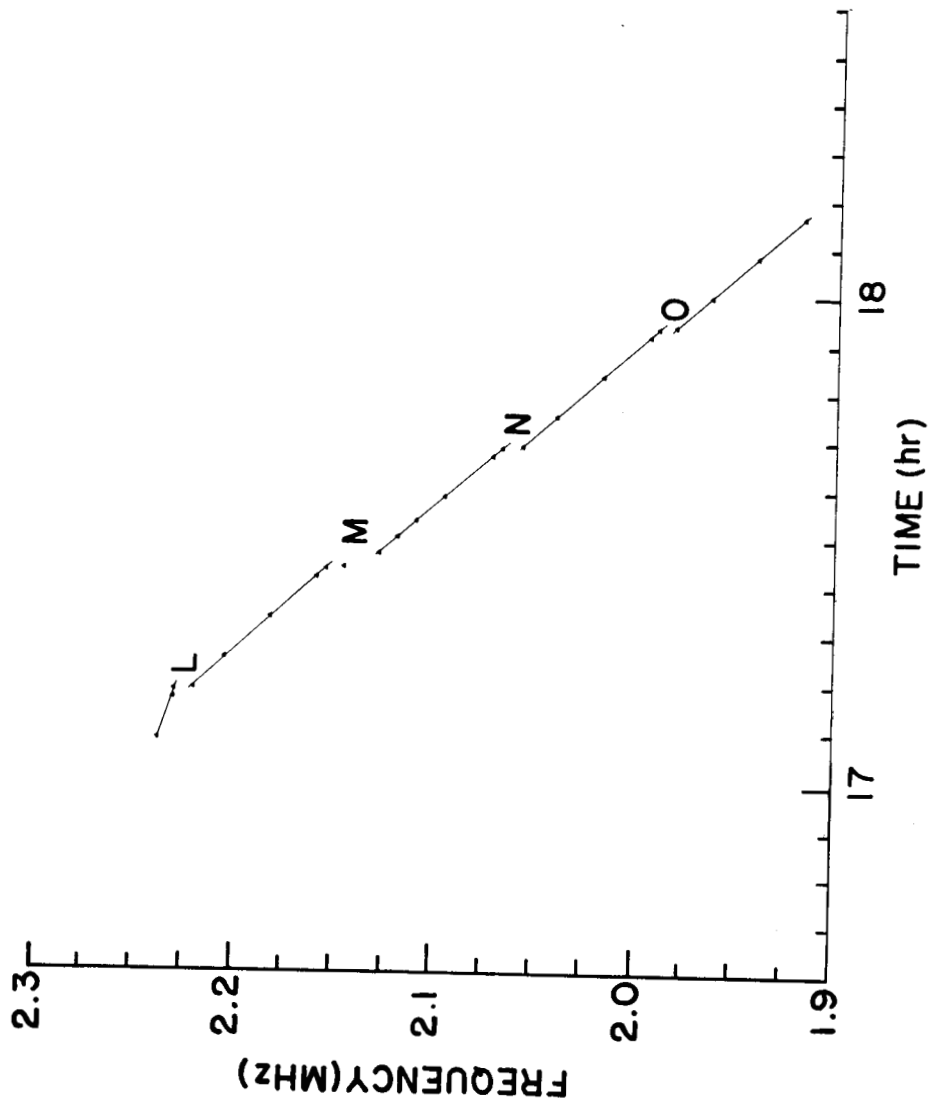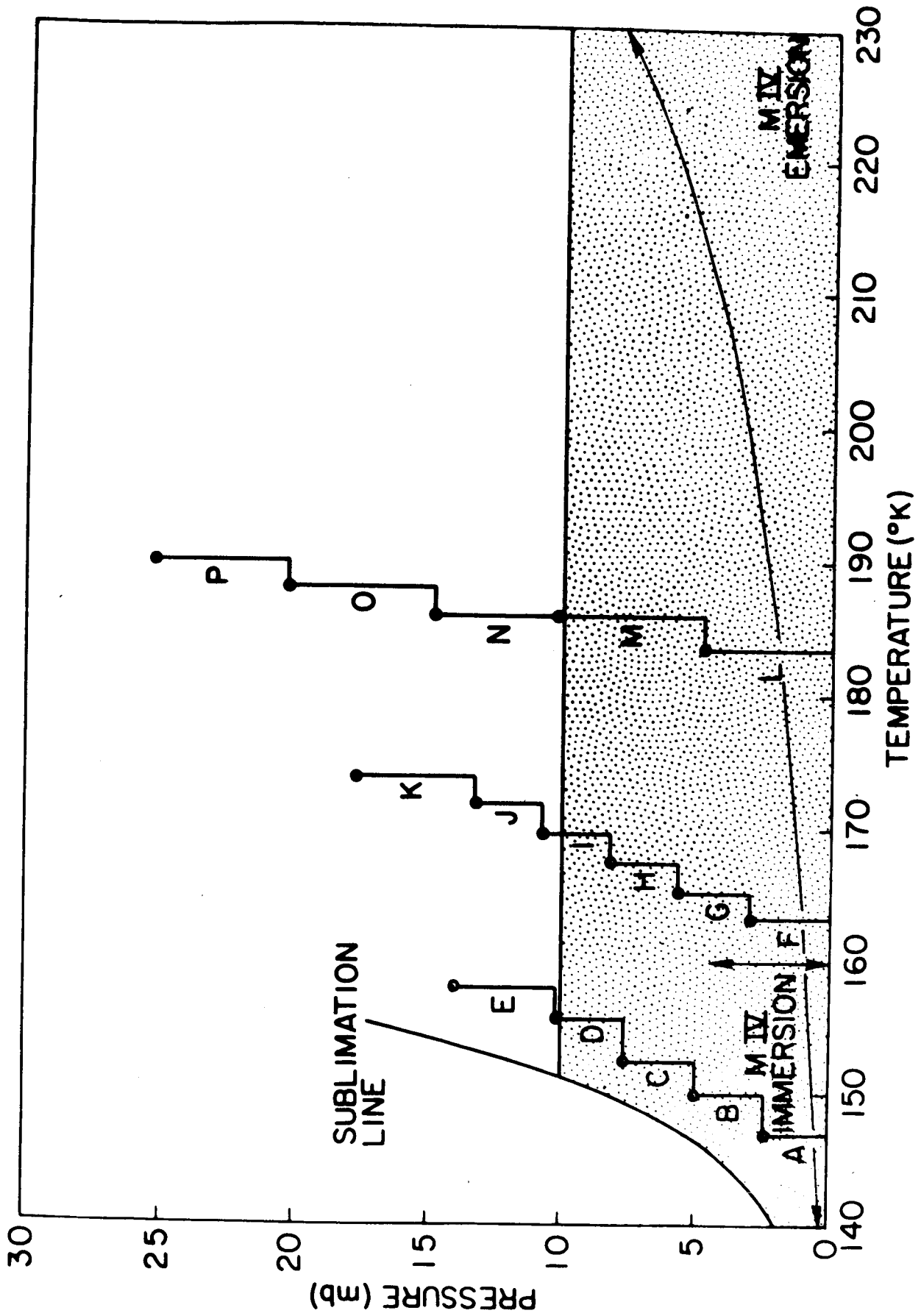5. Relationship of Measurements to Martian Conditions

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5